SOME NOTES ON COLLOIDAL CHEMISTRY AND WATER PURIFICATION[1]

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Colloidal chemistry is intimately associated with many phases of water purification. The raw water contains substances of a colloidal nature, the processes of coagulation and filtration involve colloidal phenomena, as do also those of color and iron removal. Even the destruction of bacteria by germicidal agents may be viewed in this light. As often happens with the introduction of a new science into an old and well established art, such as water purification, there has been an attempt to explain all the unsolved problems through its application, so that in a manner all that was obscure or mysterious in the water purification field has been assigned to the realm of colloidal chemistry.

Much has been said of electrical charges in colloidal chemistry and by use of this conception many of its phenomena have been explained, and a very clean cut and satisfactory theory has been evolved. But to the careful student it must appear that colloidal chemistry is rather a heterogenous collection of phenomena, which are neither physical nor chemical, and the writings of the foremost authorities seem very cautious of such a theory, excepting perhaps as a secondary effect. In many instances colloidal chemistry merely states in new language what was long known and well explained by the old chemical conceptions. This may be illustrated by the tendency to treat compound salts as adsorption products. Sometimes the explanation of phenomena by the new science and the coining of new, exotic terms seems to be carried to the point of extravagance.

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Coagulation with aluminum sulphate

Fundamental equations. Aluminum sulphate reacts with the hydroxids and carbonates of the alkali and alkaline earth metals according to the well-known equations:

1. $Al_2\ (SO_4)_3 + 3\ Ca\ (OH)_2 = Al_2\ (OH)_6 + 3\ CaSO_4$
2. $Al_2\ (SO_4)_3 + 3\ Na_2CO_3 + 2H_2O = Al_2\ (OH)_2\ (CO_3)_2 + 3\ Na_2 SO_4 + H_2\ CO_3$
3. $Al_2\ (SO_4)_3 + 3\ CaCO_3,\ H_2CO_3 + 2H_2O = Al_2\ (OH)_2\ (CO_3)_2 + 3\ CaSO_4 + 4H_2CO_3$

The equations (2) and (3) differ from the usual form in representing the precipitate as a basic carbonate instead of as the hydroxid of aluminum as in equation (1). This seems to be borne out experimentally when all products of the reaction are analyzed, as well as the precipitate. It is possible that the basic carbonate is an adsorption compound, and the loss in weight on heating above 150°C., would predispose toward the belief that the carbonic acid was adsorbed in the aluminum hydroxid as it formed. On the other hand, the sulphates can be fully accounted for in the supernatant, while the carbonic acid cannot, and there is a decided difference in the details of reaction and the appearance of the precipitate as obtained in the three cases which the equations represent. In all cases the precipitate carries additional water of hydration.

These reactions of course comport themselves with due regard to the laws of mass action as respects the effects of time, concentration and temperature, a fact which is mentioned merely because its assertive existence is obscured in the minds of some by the secondary colloidal phenomena involved.

The reactions in distilled water

When aluminum sulphate is added to solutions of sodium carbonate, hydroxide, calcium hydroxide or calcium bicarbonate of equivalent strength in distilled water, essentially free from carbonic acid, the reaction is very slow. With a temperature of 20°C., and with 10 grains per gallon of aluminum sulphate, coagulation becomes visible in one hour, and the reaction completes itself in two hours; while with lesser doses the time of reaction increases up to 5 hours for visibility when only 3 grains per gallon are used. With less than

3 grains the reaction becomes very slow, while with 1 grain no coagulation appears even after several days. The precipitate in all cases forms rather large globular flocks, almost transparent and widely separated. The rate of settling is slow, almost invisible.

It is frequently the case that great difficulty is experienced in obtaining coagulation with clear waters, especially if they are almost neutral, contain carbonic acid, or are of low temperature In such cases it is necessary to add soda ash or lime to make up for the lack of alkalinity. It may be that no coagulation occurs in the settling basins, but a finely divided floc appears in the filtered water. When this occurs the cause is treated more or less as a mystery or is vaguely attributed to colloids or to inhibitive effects. I believe it is satisfactorily explained as the natural reaction with aluminum sulphate and the equivalent of alkali in the very dilute solutions employed and that this merely follows the law of mass action. Furthermore there is no nuclear matter on which precipitation can commence. The action of carbonic acid seems to be one of retardation, as it is opposed to one of the phases of the forward reaction.

The reactions in turbid water

In turbid waters these reactions are much more satisfactory. In the case of a suspension of kaolin in distilled water, using the above equivalent amounts of aluminum sulphate and soda ash the reaction is much more rapid, and the coagulation is good and settlement rapid. Coagulation occurs with all doses from 1 grain per gallon upward, the time element being an inverse function of the size of dose. This effect may be due to the mutual precipitation of the kaolin suspension and the colloidal aluminum hydroxide, or it may be that the suspended particles of the former furnish a nucleus for the reaction.

Practically, the usual turbidity is caused by clay suspensions which at the same time impart a considerable alkalinity to the water making it unnecessary to add an alkali to a turbid water, so that much of the difficulty encountered in coagulating a clear water is avoided.

The practical measure of turbidity

A distinction should be made between turbidity and suspended matter. Such suspended matter as would settle out by plain sedi-

mentation in passing through the settling basin is of minor importance in coagulation, only insofar as it adsorbs a small amount of coagulant. On the other hand, such suspended matter as does not settle below the zone of flow while passing through the settling basin must be coagulated and represents the turbidity with which we are concerned in coagulation. It would therefore seem more logical to base the turbidity reading not on the shaken sample, but on the matter remaining in suspension at a definite time after shaking. This period of settlement in the sample should be based on the flowing-through time of the settling basin, being a definite fraction of this. I have been using 30 minutes of settling as an average value. The usual turbidity reading immediately after shaking should also be made. A comparison of the two gives an index of the character and fineness of the suspended matter.

Effect of excess of alkali on coagulation

To a series of vessels of distilled water we may add increasing amounts of an alkali or an alkaline carbonate, starting with zero at one end and finishing with say 200 parts per million at the other end. To each of the vessels an equal dose of aluminum sulphate is then added. Commencing at the zero end, increasing amounts of coagulum will be formed, reaching a maximun at the point where the amount of alkali is equivalent to the amount of aluminum sulphate, and then decreasing gradually until finally a point is reached where no coagulation occurs. I have not found a cyclic occurrence of this effect as mentioned by some writers.

It has been suggested by various writers that this failure to obtain coagulation is due to the formation of soluble aluminates according to the equation:

$$4.\ Al_2(SO_4)_3 + 6\,Na_2CO_3 + 6\,H_2O = 2\,Na_3AlO_3 + 3\,Na_2SO_4 + 6\,H_2CO_3$$

However, the same failure of coagulation is obtained with calcium hydroxide as with sodium hydroxide or carbonate, although calcium aluminate is insoluble. Furthermore, the failure to coagulate does not take place with twice the amount of alkali or calcium hydrate required for coagulation, but when the concentration of hydroxyl ions is twice that required for coagulation, which is quite another matter, as the degree of ionization enters in.

The presence of carbonic acid has the effect of increasing the amount of alkali necessary to inhibit coagulation, in that it seems to neutralize an equivalent portion of the alkali present. For this reason also the inhibition does not occur in coagulation with excess of sodium, calcium or magnesium bicarbonate. The presence of clay or turbidity partially offsets the inhibitive effect of alkali and caustic lime.

It would be instructive to study this matter in terms of hydrogen ion concentration, since evidently it is due to the free hydroxyl ions present, and does not occur when these are repressed by hydrions.

Before leaving the subject of coagulation it is well to emphasize again that most of the difficulties encountered occur with clear water. In the case of turbid water it is largely a question of adding the proper amount of coagulant. Yet there are filtration plants which must treat a highly polluted and yet clear, soft water part of the time. Unless under such conditions coagulants are used in large amounts, passably good bacterial efficiency cannot be obtained and the use of the necessary amounts is usually discountenanced by municipal authorities, because of the excessive operating cost engendered. With such limitations, partly physical and partly economic, it is not logical to expect satisfactory results, and it should be recognized that a portion of the burden borne by filter plants under more normal conditions must then be shifted to chlorination. Usually the pollution factor under such conditions can be traced to direct introduction of sewage into the raw water at some point above the plant, and an active policy of sewage purification is indicated. By clear water in the above sense is meant water from small streams in dry weather or in large canalized streams, rather than supplies such as the Great Lakes, which contain a slight trace of turbidity and sufficient salts to materially assist coagulation.

It should be recognized then that with clear, soft (and in certain cases acid) waters, carrying a high bacterial pollution, and perhaps some of the organic colloids associated with sewage, rapid sand filtration is not an unqualified success, because its effectiveness depends on coagulation, which is difficult to obtain under these circumstances, either with alum alone or with the addition of lime or soda ash. Long reaction periods, fine sand and deep layers thereof in the filters, and low rates of filtration are of some value. Sources of sewage pollution in the raw supply should be traced out and

corrected by disposal works and disinfection. But even with these remedies recourse must generally be had to chlorination, not as an additional safeguard, but as an essential element of the purification process.

Color and coagulation

It is almost needless to say that in speaking of color in water, true color is meant and not that due to iron or to the apparent color imparted by turbidity or suspended matter. The usual colored water has a clear yellow or brownish tinge, which is not removed by passing through filter paper. It is usually found in clear soft water, and manifests its peculiar properties best in such water. It may also be present in turbid water either coexistent with the turbidity or as part of the vegetable matter in the clay, but under such conditions is less troublesome or may even pass unnoticed because of the clay suspension predominating in the behavior and reactions of the water. Whenever color is present, certain peculiarities and difficulties in coagulation occur and must be overcome to effect its removal.

Water acquires color thru contact with decaying vegetation in swamps, sluggish streams or reservoirs. The coloring matter is of a complex organic nature, consisting of tannates and gallates, glucosides of gallic and other organic acids; substances having certain characteristic properties in common. In some ways they resemble the alums of inorganic chemistry, being strong astringents, precipitating gelatine, and behaving similarly toward certain dyes. They derive their name from association with the tanning industry. For the sake of simplicity, I will confine myself to tannic acid, the other tannins having very similar properties. In some instances my observations have been at variance with those given in chemical books, which may be due to the fact that in water purification the solutions dealt with are very dilute.

Tannic acid

Tannic acid, also called gallo-tannic or digallic acid, in a pure state is a light brown, flaky powder. It dissolves very readily in water, giving a colorless solution, which soon turns yellow. My experiments indicate that the color change is due to light, and not to oxidation, since solutions containing no air or carbon dioxide

quickly turn yellow on exposure to the sun, but if kept in darkness, do not color, even if aerated or saturated with carbon dioxide. Tannic acid solutions exhibit colloidal properties, as may be shown by dialysis and in other ways. In structure it is formed of two molecules of gallic acid joined together with separation of water. Gallic acid is trihydroxybenzoic acid. Consequently the formula of tannic acid is $C_{14}H_{10}O_9$. The colored solution which develops on exposure to light is meta-tannic acid. That is, the light effects an internal rearrangement in the atoms of the tannic acid molecule. From its structure, tannic acid contains one replaceable acid hydrogen, and in many reactions this is replaced by a metal or other positive radical just as would occur with a simple inorganic acid, such as carbonic acid. It is only slightly ionized, being barely within the acid range of methyl orange, but falls well within the phenolphthalein range, which is a good indicator to use. Incidentally, for this reason, colored waters may show an erroneously high CO_2 reading. With calcium hydroxid, sodium hydroxid, carbonate and bicarbonate, and with calcium and magnesium bicarbonates, that is, with salts which in the generally accepted sense are alkaline, it forms opalescent, brown or greenish solutions of a colloidal nature. It does not react with sodium, calcium or magnesium sulphates and chlorides, and in dilute solutions, hydrochloric or sulphuric acids do not precipitate it. With metallic sulphates a precipitate forms, which with iron sulphate is dense and bluish black, and with aluminum sulphate, rather meager, flocculent and of lavender color.

Color in water

As just mentioned, solutions of tannic acid turn yellow on exposure to light. On the addition of alkaline salts of sodium, calcium or magnesium, the solution becomes a pronounced brown, and at times has a greenish cast, especially with magnesium. Light accelerates this reaction, but is not essential. It may be stated that the resulting color is due to the tannates formed, since the production of an equivalent amount of carbonic acid in the case of carbonates indicates an actual interchange, but certain facts encountered in color removal incline toward the color as being due to tannic acid in presence of alkalis. The intensity of color is proportional to the amount of alkaline salt present. These colored tannate solutions exhibit the same colloidal properties as does tannic acid.

Color removal with aluminum sulphate

A. Acid color. As suggested previously, when aluminum sulphate in amounts from 1 to 20 grains per gallon is added to tannic acid solutions of such strength as occur in natural waters, a flocculent, lavender precipitate is formed in all cases. The reaction is slow, requiring about 24 hours or more. Exposure to light and air are necessary for its occurrence. Although neither tannic acid nor aluminum sulphate gives more than a faint indication of acidity with methyl orange, the supernatant liquid after this reaction is decidedly acid to this indicator. This residual acidity is equal to the equivalent of the tannic acid originally present. Since the supernatant liquid does not contain aluminum nor react to tests for tannic acid, it seems reasonable to suppose that the reaction depends on the hydrolysis of the aluminum sulphate, the combination of the slightly hydrolyzed aluminum hydroxide with the tannic acid to form what in dyeing is termed a "lake," which precipitates, leaving free sulphuric acid in solution. The low speed of reaction favors this view also. Because of the dilute solutions and the known effect of light on some organic compounds, such a possibility seems less unreasonable than would otherwise be the case.

B. Alkaline color. If equal quantities of an alkaline colored water are poured into a series of vessels, and aluminum sulphate is added to each vessel, the amount added increasing from vessel to vessel, the results observed are interesting. The several vessels having the lowest dose of aluminum sulphate retain their clear brown color, the following vessels become opalescent, but no precipitate is thrown down, then further along in the series there is a point where coagulation takes place. This point is well defined, all vessels containing less coagulant do not coagulate, and all vessels containing more coagulant, coagulate very thoroughly and leave a clear supernatant. By careful manipulation this critical point can be located to within 0.1 grain per gallon of coagulant, that is, a dosage of alum can be found such that no coagulation takes place, but addition of a tenth grain more will cause complete coagulation. The floc that forms is very coarse, flocculent, and settles readily. It is light brown in color. Coagulation and settlement occur most rapidly at slightly above the critical point, but as the amount of coagulant increases the reaction becomes slower. I have added excess coagulant in varying amounts up to twice the critical value, under which condition the reaction became very slow, but eventually clarification resulted.

The position of the critical point is as follows:

If the amount of soda ash or other alkali present is equivalent to the amount of tannic acid present, then coagulation occurs when the amount of aluminum sulphate added is equivalent to the tannic acid present (and of course also equivalent to the soda ash present).

If the amount of soda ash or other alkali present is more than equivalent to the amount of tannic acid present, then coagulation also occurs when the amount of aluminum sulphate added is equivalent to the tannic acid present, but the color is only partly removed, and additional amounts of aluminum sulphate effect a proportionate reduction of the residual color, until with an amount of aluminum sulphate equivalent to the total soda ash present, complete color removal occurs.

If the amount of soda ash or other alkali present is less than equivalent to the amount of tannic acid present, then coagulation occurs when the amount of aluminum sulphate added is equivalent to the amount of soda ash present, giving a clear supernatant, but with larger amounts of coagulant, larger amounts of precipitate are obtained.

This may be better formulated, so as to give an insight into the internal mechanism as follows:

a. Alkali exceeding twice tannic acid. The aluminum sulphate added combines with the free alkali to form aluminum hydroxide, which is inhibited from precipitating by the tannic acid, until an equivalent amount has formed. At this point coagulation commences, further addition of aluminum sulphate combining with the remaining free alkali and then with the alkaline tannate to form tannic acid and aluminum hydroxide, which precipitate, releasing and precipitating an equal amount of the aluminum hydroxide previously formed, so that after the critical value there is a gradual removal of color.

b. Alkali twice tannic acid or less. The aluminum sulphate added combines with the free alkali to form aluminum hydroxide, which is inhibited from precipitating by the tannic acid until an equivalent amount has formed. At this point coagulation commences, and additional aluminum sulphate combining with the tannate precipitates, and releases an equal amount of the aluminum hydroxide already formed, which also precipitates, so that after the critical value there is a gradual removal of color, and at twice the critical value all the color is removed.

c. Alkali equal to tannic acid. Aluminum sulphate added combines with the alkali from the tannate forming aluminum hydroxide and tannic acid in equal amounts, resulting in inhibition until an amount of aluminum hydroxide equivalent to the tannic acid has been formed. A slight addition of aluminum sulphate beyond the critical value causes complete coagulation and color removal. If aluminum sulphate in excess is added, the rate of reaction decreases in proportion to this excess, probably because a basic sulphate of aluminum and tannic acid are first formed, later being precipitated by hydrolysis as described under "Acid Color."

d. Alkali less than twice tannic acid. Aluminum sulphate added combines with the alkali from the tannate forming aluminum hydroxide and tannic acid in equal amounts, inhibition resulting until all the alkali has been used up in this way. This is the critical point, at which coagulation occurs, and all color is removed. Additional aluminum sulphate causes additional precipitate with the residual tannic acid, as described under "Acid Color."

It is difficult to make a perfectly satisfactory general statement of these reactions, but it is possible to visualize the conditions mentally after studying a number of concrete cases. In the instances considered the components: alkali, aluminum sulphate, and tannic acid enter in; in every case there is the inhibition between aluminum hydroxide and tannic acid, and the final product of a mixed precipitate of aluminum hydroxide and tannic acid, with in some cases an after precipitate of an aluminum tannate. Probably the two precipitates are identical in character, which partakes of that of the "lakes" of the dyeing and paint industries. It is evident that carbonic acid may enter in to change the critical point, as explained under coagulation, and probably also other factors not here considered.

Color removal in practice

Colored water may be clear, with a yellowish tinge, or it may appear turbid, in which case its true character may be obscured by the seeming "colloidal turbidity." It has a varying alkalinity, but usually a rather high CO_2 reading, due in part to organic acid. If treated experimentally with aluminum sulphate, there will always appear a critical point at which coagulation commences. If no such critical point occurs, the color, if present at all, is not of practical importance, it being then merely a question of turbidity removal.

Not only the amounts of alkalinity and coloring matter, but their relative proportions must be considered if complete removal is desired. If the alkalinity exceeds or equals the coloring matter then sufficient aluminum sulphate must be added to combine with the total alkalinity. If the alkalinity is less than the coloring matter, then an amount of aluminum sulphate must be added to combine with the total coloring matter, and sufficient lime or soda ash added to supply the deficit between the coloring matter and alkalinity. This assumes that a complete removal of color, as well as tannic and other organic acids is desired. If merely enough coagulant is used to effect coagulation at the critcial point or to remove the colored tannates, gallates, etc., a pale but persistent color will reappear due to the action of light upon the free tannic acid remaining in solution. This is the "residual color" which is mentioned in the literature on the subject as being so difficult to overcome. As just indicated its speedy removal requires equivalent amounts of both aluminum sulphate and lime or soda ash. Besides a careful estimation and application of coagulants, color removal requires adequate time, which means amply large coagulation basins.

The test for color and tannins in water

I feel that the present method of testing and recording color is insufficient. It is at best the record of a physical impression. The shade and depth of color does not measure the true value of the components which are the causative factors, nor does it furnish a proper working basis for treatment. Thus a water containing a large amount of tannic acid and a low alkalinity would give a less color value than one in which the reverse were true, although the former would manifest more strongly the peculiar characteristics associated with color, and would require the more complete color treatment. While the present color test gives desirable physical data, there should be tests which will give the free and combined alkalinity, and the total acids of the tannic group. The usual indicators, methyl orange and phenolphthalein, are handicapped by the color already present, and in the case of the latter by the fact that it would indicate carbonic acid as well as the organic acids desired. As to possible methods, a coagulation test for the critical point, or titration against hide powder to determine the tanning value suggest themselves. Other lines of attack may be in the determination of organic

solids in the evaporated sample, permanganate titration or an electrolytic method for determining total acidity regardless of color changes.

As this question of color affects many turbid waters we cannot make much progress in improving the methods of coagulating such waters, or determine the coagulant needed on a rational basis, until better means for estimating color are available.